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Electrical Characteristics of Anatase-TiO_2 Films by Low Temperature Fabrication

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1. Introduction

It has been reported that CMOS fabricated by the gate-last process at a low temperature are being mass produced. Future scaling of CMOS technology requires a higher-k dielectrics (k >30). Several approaches have been reported to obtain cubic-HfO_2 with a high k value by specific annealing process with fast ramping-up [1, 2]. TiO_2 is one of the most promising candidates of higher-k materials because of a high k value and low temperature crystallization. In this paper, we present characterization of anatase-TiO_2 films fabricated by ALD and PDA processes, and discuss the Vfb change due to oxygen transfer in TiO_2 film by annealing in oxidation and reduction conditions.

2. Experimental

The TiO_2 films with 3-6 nm thicknesses were deposited on SiO_2/Si(100) and SiO_2/Si(111) by the ALD process at 200 ºC using $Ti(NMe_2)_4$ precursor and H_2O gas. The PDA was performed at 300-500 °C for 30 sec in O_2. TiO_2 MOS capacitors with TaC and Pt gate electrodes were fabricated. MOS capacitors with Al_2O_3 and HfO_2 dielectrics were also prepared to discuss the Vfb shift. All capacitors were annealed at 400 °C in 3% H_2 (FGA). The oxygen transfer in TiO_2 layer was controlled by using the catalytic effect of the Pt as follows: To remove oxygen from TiO_2 layer, FGA was carried out at 400-500 °C in 3% H_2. To introduce oxygen into TiO_2 layer, oxidation annealing (ODA) was performed at 100-300 °C for 1-200 min in O_2.

3. Results and Discussion

3.1 Physical characterizations of TiO_2 films

The peaks of C and N impurities in as-deposited TiO_2 film are undetectable by angle-resolved XPS analysis, as shown in **Fig. 1**. The typical XRD patterns of as-deposited and annealed TiO_2 films are shown in **Fig. 2**. We found that the TiO_2 film consists of anatase structure at temperature above 300 °C. **Fig. 3** shows capacitance equivalent thickness (CET) as a function of TiO_2 thickness on Si(100) and Si(111). The anatase-TiO_2 films were prepared by PDA at 500 °C. The k values in Si(100) and Si(111) samples are estimated 35 and 32, respectively. This demonstrates that the anatase-TiO_2 films which formed at low annealing temperature (500 °C) show a significant high k value (>30).

3.2 Vfb shift due to oxygen transfer in TiO_2 layer

Fig. 4 shows C-V characteristics of TaC-gated MOS capacitors with SiO_2, TiO_2, HfO_2 and Al_2O_3 dielectrics. The C-V curve of TiO_2 capacitor slightly shifts toward positive direction in comparison with SiO_2 capacitor. **Fig. 5** summarizes Vfb behaviors of several high-k dielectrics. All high-k dielectrics occurs positive Vfb shift compared with SiO_2. Note that the value of the positive Vfb shift in high-k dielectrics can be ordered as follows: Al_2O_3 (0.72 V) > $HfSiO_x$ (0.36 V) [3] > HfO_2 (0.29 V) > TiO_2 (0.08 V). It is well known that the Vfb shift of high-k CMOS predominantly occurs due to the bottom interface dipole at high-k/SiO_2 interface [4, 5]. A schematic illustration of band diagram of TaC/high-k/SiO_2/Si stack structure is shown in **Fig. 6**. The Vfb shift of each dielectric relates to the strength of the bottom interface dipole of each one.

Fig. 7 shows the relationship between the normalized Vfb and the ODA temperature for TiO_2 MOS capacitors with Pt and TaC gate electrodes. The Vfb of the Pt-gated MOS capacitors shifts in the positive direction as the ODA temperature increases, while the Vfb of TaC-gated MOS capacitors shows an almost constant value. No difference of the C-V curve and Vfb behaviors between Si(100) and Si(111) samples appears regardless of the ODA temperature. This indicates that the orientation of Si substrate doesn't affect to the Vfb shift. To investigate the influence of the oxygen transfer in the TiO_2 layer on the Vfb shift, we examined the annealing time dependence of the Vfb shift, as shown in **Fig. 8**. The C-V curves of capacitor shift in the positive direction with increasing the annealing time (an inset graph). The Vfb change in ODA at 250 °C saturates at ODA times above 4 min. In contrast, none of the Vfb value in ODA at 150 °C is saturated even after annealing for 200 min. These results suggest that the oxygen diffusion in TiO_2 layer affects to the Vfb shift as previously reported [6]. **Fig. 9** shows the change of Vfb for TiO_2, HfO_2 [6] and $HfSiO_x$ [6] dielectrics after ODA at 300 °C and FGA at 500 °C. The positive and negative Vfb shifts for all samples appear in ODA and FGA treatments, respectively. We found that the TiO_2 dielectric shows the maximum and minimum Vfb change after ODA and FGA, respectively. This strongly indicates that the oxygen transfer of the TiO_2 dielectric is faster than those of HfO_2 and $HfSiO_x$ dielectrics.

4. Conclusions

We demonstrate that anatase-TiO_2 films, which formed in low temperature fabrication process, show a significant high dielectric constant of 35. We found that the Vfb of TiO_2 capacitor shifts slightly toward positive direction in comparison of SiO_2. Note that the oxygen transfer in TiO_2 layer relates to the Vfb shift from results in ODA and FGA.

References

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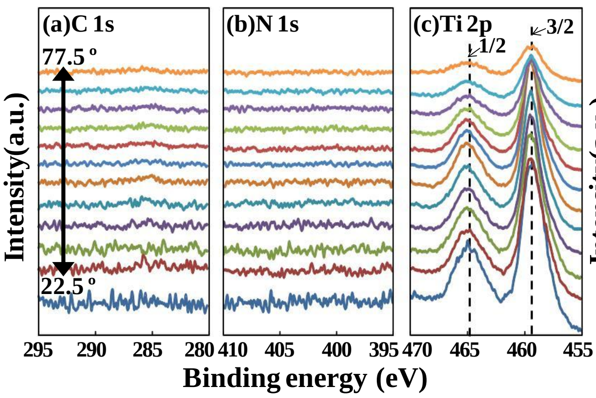

Fig. 1. Angle-resolved XPS spectra of (a)C1s, (b)N1s and (c)Ti2p in as-deposited ALD-TiO_2 film. The C1s and N1s peaks of ALD-TiO_2 film are undetectable.

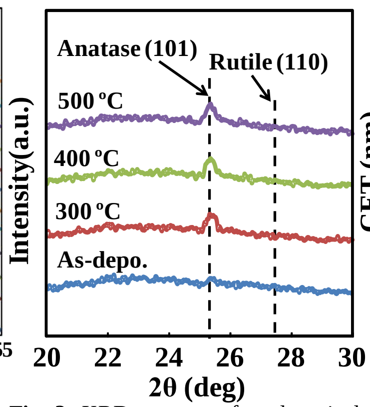

Fig. 2. XRD patterns of as-deposited and annealed TiO_2 films. The PDA was carried out at 300-500 °C in O_2. The anatase phase appears at temperature above 300 °C.

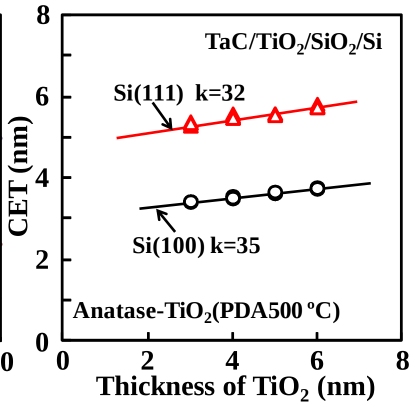

Fig. 3. The CET values as a function of thickness of anatase-TiO_2 films on SiO_2/Si (100) and SiO_2/Si(111). The k values of Si(100) and Si(111) samples are estimated 35 and 32, respectively.

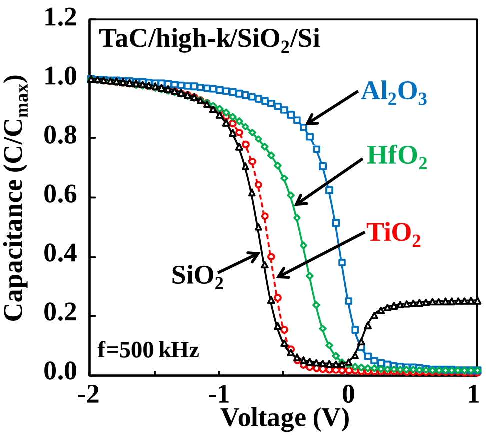

Fig. 4. The C-V characteristics of TaC-gated MOS capacitors with SiO_2, TiO_2, HfO_2 and Al_2O_3 dielectrics. The C-V curve of TiO_2 capacitor slightly shifts towards positive direction compared to SiO_2 one.

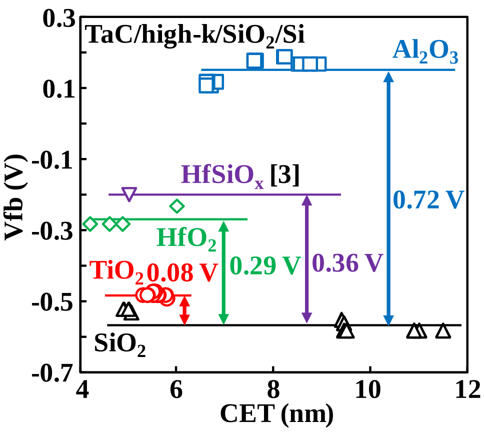

Fig. 5. The Vfb behaviors of SiO_2, TiO_2, HfO_2, Al_2O_3 and $HfSiO_x$ [3] dielectrics. The value of the positive Vfb shift in high-k dielectrics can be ordered as follows: Al_2O_3 (0.72 V) > $HfSiO_x$ (0.36 V) > HfO_2 (0.29 V) > TiO_2 (0.08 V).

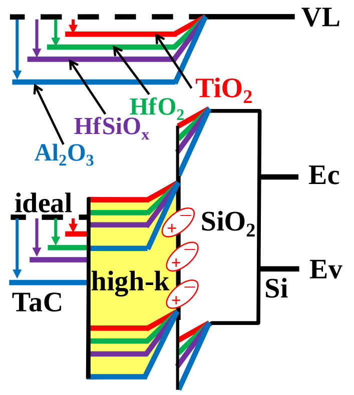

Fig. 6. Schematic band diagram of TaC/high-k/SiO_2/Si stack structure. The strength of the bottom interface dipole in high-k can be ordered as follows: Al_2O_3 > $HfSiO_x$ > HfO_2 > TiO_2.

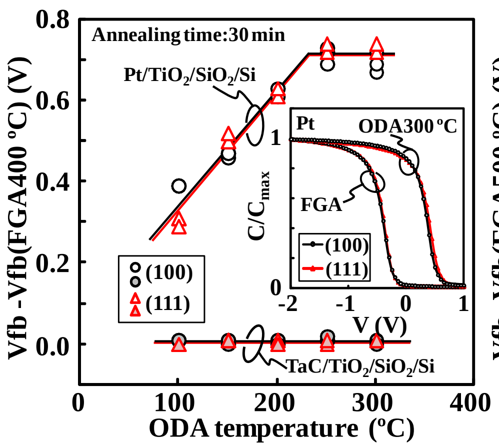

Fig. 7. Normalized Vfb versus ODA temperature for TiO_2 MOS capacitors with Pt and TaC gate electrodes. An inset graph shows C-V curves of Pt-gated MOS capacitors after FGA and ODA at 300 °C. No difference of Vfb between Si(100) and Si(111) samples appears.

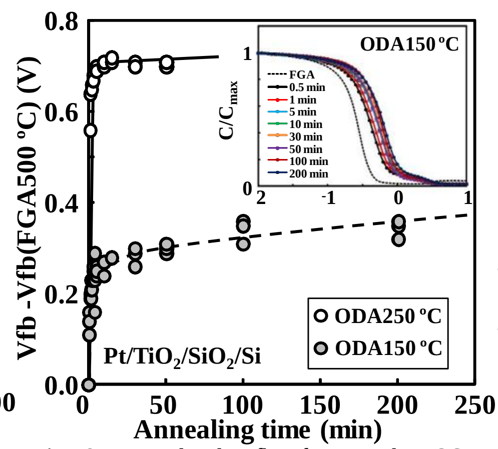

Fig. 8. Normalized Vfb of Pt-gated MOS capacitors as a function of annealing time. An inset graph shows C-V curves of capacitor in ODA 150 °C. The change of Vfb in ODA at 150 °C doesn't saturate even at ODA times 200 min.

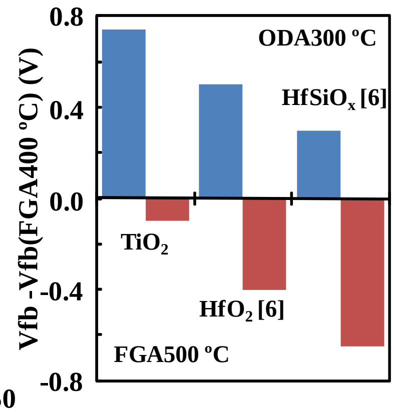

Fig. 9. The change of Vfb for TiO_2, HfO_2 [6] and $HfSiO_x$ [6] dielectrics after ODA at 300 °C and FGA at 500 °C. The TiO_2 dielectric shows maximum positive Vfb shift and minimum negative Vfb shift after ODA and FGA, respectively.